Estimation of Analytical Measurement Uncertainty

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Introduction

- Analytical measurement uncertainty
  - ISO 17025 requirements
- Rationale for estimating uncertainty
  - Guide to the Expression of Uncertainty in Measurement (ISO GUM)
- Nested approach
  - Based on quality control data

National Environmental Laboratory Accreditation Conference

- NELAC Chapter 5 based on ISO/IEC 17025
- ISO/IEC 17025 replaces ISO Guide 25
- General Requirements for the Competence of Testing and Calibration Laboratories
- Guide to the Expression of Uncertainty in Measurement (ISO GUM)
- American National Standard Institute for Expressing Uncertainty (ANSI GUM)

ISO 17025 References to Uncertainty

- References uncertainty in:
  - 4.12.2.1
  - 5.1.2
  - 5.4.1
  - 5.4.6.1
  - 5.4.6.2
  - 5.4.6.3
  - 5.6.2.1.1
  - 5.6.2.2.1
  - 5.10.3.1
- Where applicable, include a statement on the estimation of uncertainty of measurement with results
- Instead of reporting: *10 mg/L,*
  Now report: *10 +/- 2 mg/L @ 95% CL*

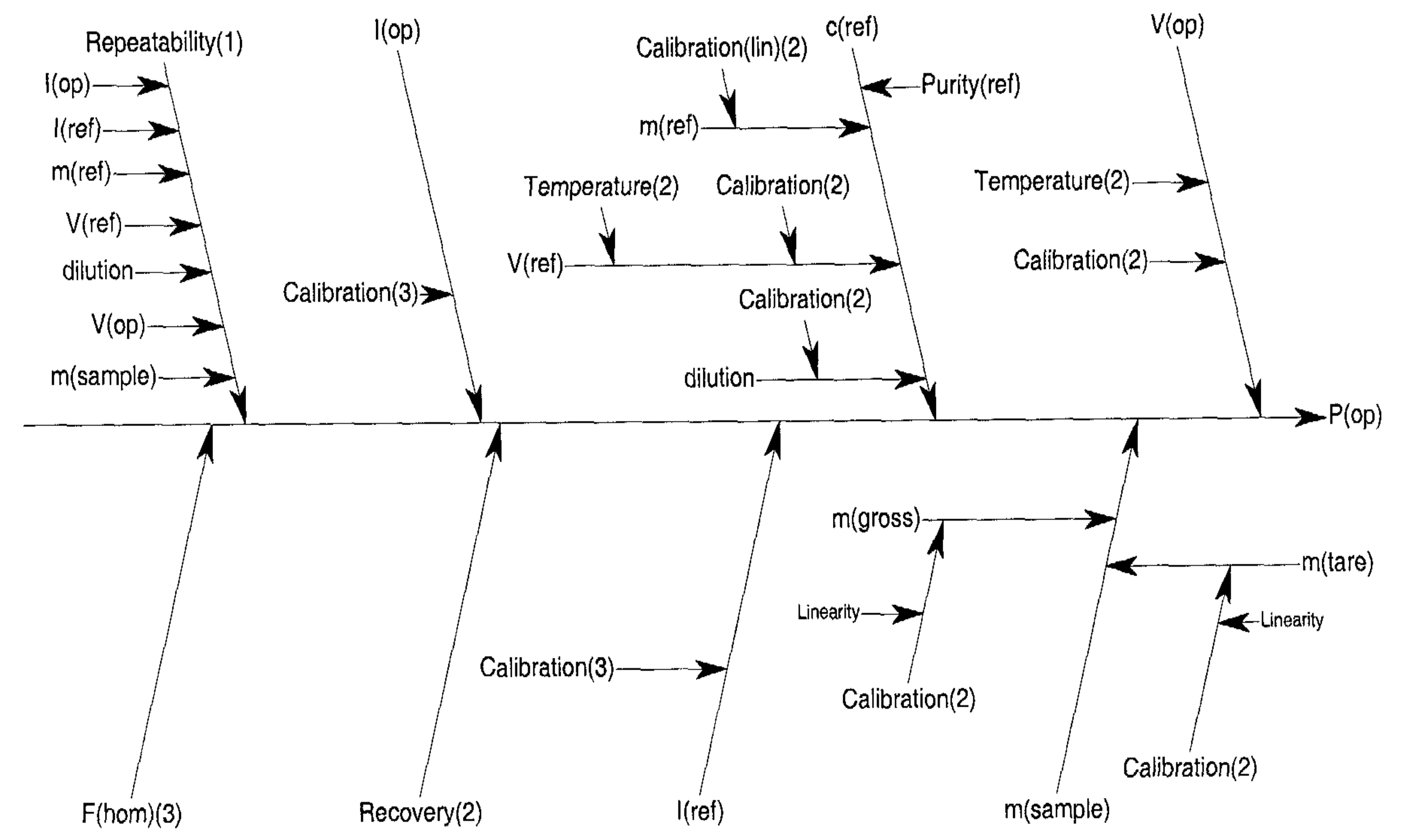
GUM: Systematic Estimation of Measurement Uncertainty

- Identify the analytical components of uncertainty
- Represent the standard uncertainties by the standard deviations of the components
- Evaluate the covariance of the components that contribute to uncertainty
- Combine the standard uncertainties of the analytical components
- Expand the combined standard uncertainty

Approaches

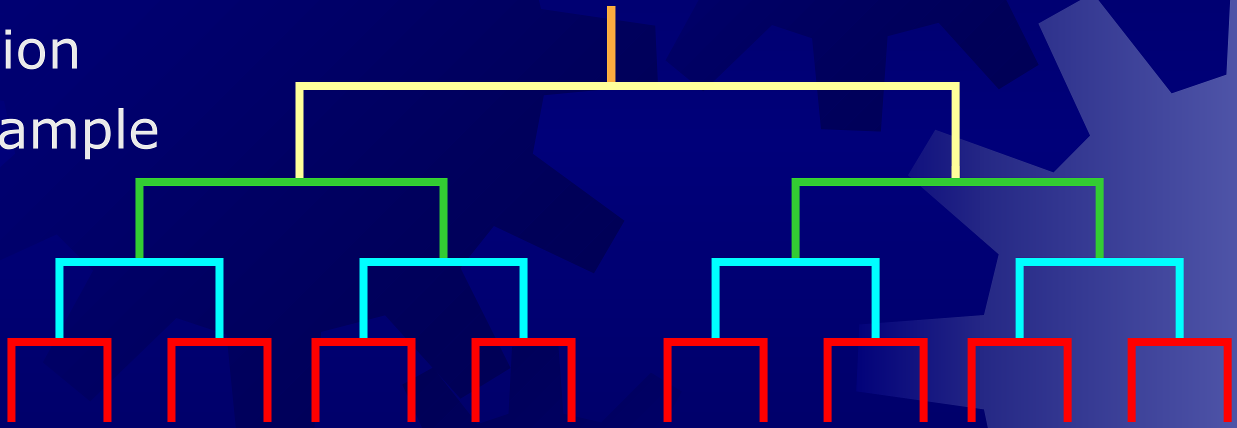
- EURACHEM
- Fully-nested hierarchical analysis of variance
- PT approach
- LCS approach
- Nested approach based on QC data

EURACHEM Approach



Fully-Nested Hierarchical Design

- Sample Location
- Co-Located Sample
- Field Split
- Preparation
- Test



Fully-Nested Hierarchical Design

- Conventional five factor fully-nested design
- Provides too little information on the upper levels
- Provides more than enough information at the lower levels
- For every 1 sample, there are 16 analytical measurements

PT and LCS Approaches

- Proficiency testing (PT) control limits
  - Matrix specific
  - Do not represent specific laboratory
- LCS control limits
  - Generated in-house from historical laboratory data
  - Do not represent matrix interference

Total Study Variability: *Hierarchy of Components*

- TOTAL STUDY VARIABILITY
  - STUDY POPULATION
  - CO-LOCATED SAMPLE
    - SAMPLING DESIGN
    - FIELD SPLIT SAMPLE
      - FIELD SAMPLE COLLECTION
      - MATRIX DUPLICATE SAMPLE
        - SAMPLE PREPARATION
        - CALIBRATION STANDARD

Components of Total Study Variability

- Study population
- Sampling design
- Sample collection
- Sample preparation
- Matrix interference
- Laboratory testing

Study Population Effects

- The natural variability inherent in the contaminant distribution of the sampling site
- Cannot be reduced, but can be estimated
- Estimated natural variability confounded by sampling and testing uncertainty

Sampling Design Effects

- Design strategy
  - Number of samples
  - Location of samples
- Simple random sampling
- Stratified random sampling
- Systematic grid sampling
- Composite sampling
- Representativeness of sampling

Sample Collection Effects

- Sample collector efficiency
  - % Recovery of analytes
  - Bias is controlled when every particle has the same probability of being selected
- Sample collector decontamination
  - Cross-contamination from one sample location to the next
- Sample preservation
  - Degradation or precipitation of analytes

Sample Preparation Effects

- Homogenization, particle size reduction, and subsampling
- Extraction, separation, and concentration
- Percent recovery of analytes from each preparation process

Matrix Interference Effects

- Refractory matrices
  - Inhibit extraction of analytes
- Co-precipitation of interferents
  - Swamps analytes during concentration and separation processes
- Co-elution of interferents
  - Impacts analytical method selectivity

Test Measurement Effects

- Carryover between sample tests
- Instrumental drift
- Intrinsic instrumental repeatability
- Irreducible measurement uncertainty

Propagation of Uncertainty

- Mathematical model: square root sum of squares equation
- Laboratory analytical measurement uncertainty: ${}^{L}S_r$
  - Preparation uncertainty: ${}^{P}S_r$
  - Testing uncertainty: ${}^{M}S_r$
- ${}^{L}S_r^{\,2} = {}^{P}S_r^{\,2} + {}^{M}S_r^{\,2}$
- Example:

$${}^{L}S_r^{\,2} = (30.0\%)^2 + (10.0\%)^2$$

$${}^{L}S_r = 31.6\%$$

QC-Based Nested Hierarchical Approach

- Identifies sources of uncertainty from field sampling to laboratory testing
- Works backward
  - Backs-out component standard uncertainties from combined uncertainties of quality control samples

Conceptual Model

Sample Collection Effects (SCE)

Matrix Interference Effects (MIE)

Prep Method Effects (PME)

Spike Preparation Effects (SPE)

Intrinsic Measurement Effects (IME)

Instrument Calib Std (ICS)

Initial Calib Verification Std (ICV)

Lab Control Sample (LCS)

Matrix Interfere(Spike) Sample (MIS)

Field Duplicate Sample (FDS)

Uncertainty Calculator

- Uses readily available QC data
  - ICS, ICV, LCS, MIS (MS/MSD)
- Calculates individual contributions to measurement uncertainty
  - Excel-based
- Provides result and specifies confidence level
- Calculates relative uncertainty and uncertainty interval
  - Provides bias-corrected values (if required)

Calculation

- $((X_i - R)/R)*100$
  - X_i - Individual analytical measurement
  - R - Reference value
  - Multiplied by 100
- % deviation of analytical measurement from analyte concentration

Analytical Measurement Uncertainty Calculator

What is the analyte and matrix? Copper in Wastewater

Enter 20 replicate results for the following quality control samples as percent deviation (%):

ICS - Instrument calibration standard

ICV - Second source calibration verification standard

LCS - Laboratory control sample

MIS - Matrix interference sample (matrix spike, organic surrogate, radiochemcal tracer)

FDS - Field-split duplicate sample

CLS - Co-located duplicate sample

	ICS	ICV	LCS	MIS	FDS	CLS
	1.1	0.5	4.0	12.0	0.0	0.0
	0.8	0.1	0.5	1.4	0.0	0.0
	0.4	1.0	1.5	8.0	0.0	0.0
	2.0	1.2	1.7	3.7	0.0	0.0
	1.0	0.2	0.1	12.0	0.0	0.0
	1.2	0.4	2.2	0.4	0.0	0.0
	1.7	1.2	0.4	3.6	0.0	0.0
	3.7	0.9	0.3	0.1	0.0	0.0
	1.1	0.1	0.5	2.7	0.0	0.0
	3.1	1.3	15.0	17.0	0.0	0.0
	2.0	0.9	20.0	30.0	0.0	0.0
	0.7	1.0	0.4	3.7	0.0	0.0
	0.4	2.0	4.0	1.5	0.0	0.0
	0.9	0.2	0.6	5.0	0.0	0.0
	1.4	1.0	1.5	1.4	0.0	0.0
	1.9	1.4	5.0	20.0	0.0	0.0
	2.0	1.5	24.0	3.5	0.0	0.0
	1.5	1.7	3.0	5.0	0.0	0.0
	1.6	3.0	13.0	-24.0	0.0	0.0
	1.1	3.1	11.0	-13.0	0.0	0.0
Std. Dev.	0.84	0.85	7.2	11.1	0.0	0.0
Bias	1.5	1.1	5.4	4.7		
Recovery	101.5	101.1	105.4	104.7		

Analytical Measurement Uncertainty Calculator *Copper in Wastewater* Page 2

Components of Analytical Uncertainty
IME - Intrinsic instrumental measurement effects
SPE - Spike preparation effects
PME - Preparation method effects
MIE - Matrix interference effects
SCE- Sample collection effects
SLE - Sample location effects

Component Percent Standard Uncertainty

IME	~	0.8	% relative standard deviation
SPE	~	0.1	% relative standard deviation
PME	~	7.1	% relative standard deviation
MIE	~	8.5	% relative standard deviation
SCE	~	0.0	% relative standard deviation
SLE	~	0.0	% relative standard deviation

Component		Percent Recovery	Component		Systematic Error	
IME	~	101	IME	~	1	percent
SPE	~	100	SPE	~	0	percent
PME	~	104	PME	~	4	percent
MIE	~	99	MIE	~	-1	percent

What is the Confidence Level (CL)? Enter ONLY one of these percentages: 80, 90, 95, 99 — 95 %

Your specified t-value is 2.093 for a Two-Tailed Normal Distribution Confidence Interval

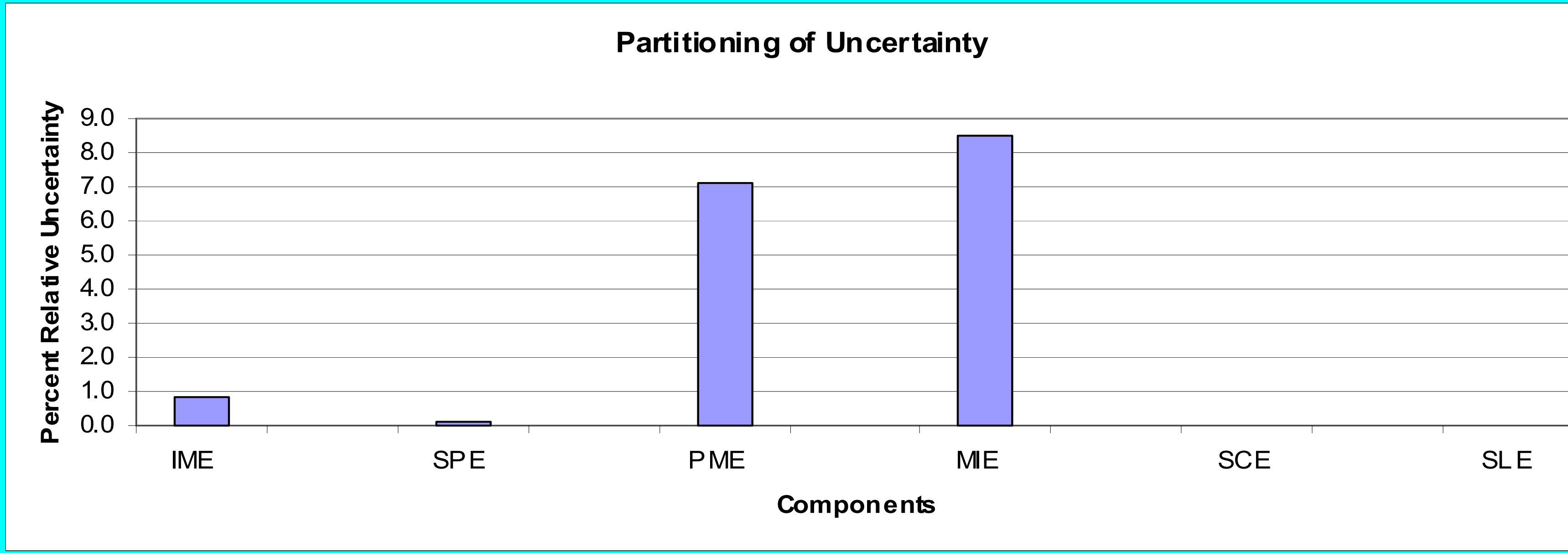
Relative Analytical Measurement Uncertainty for routine field samples
(Only the IME, PME, and MIE are combined for the analytical measurement uncertainty)

23.3	% relative uncertainty

Relative Systematic Error associated with the measurement of routine field samples
(Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error)

5.1	% relative systematic error

Analytical Measurement Uncertainty Calculator *Copper in Wastewater* PAGE 3



What is the measurement result? 10

What are the measurement units? mg/L

If the sample measurement is 10 mg/L ,
then the uncertainty interval is 7.7 - 12.3 mg/L at the 95 % Confidence Level (Expanded Uncertainty)

For the above result, if the systematic measurement error (bias) is corrected,
then the uncertainty interval is 7.3 - 11.7 mg/L at the 95 % Confidence Level (Expanded Uncertainty)

Summary

- Analytical measurement uncertainty
- Approaches
- Nested approach
- Partition and propagation of analytical measurement uncertainty

For Additional Information

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